

Classifying and reducing errors in density functional calculations

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The energy error of any DFT calculation can be decomposed into a contribution due to the approximate functional and that due to the approximate density. Typically, the functional error dominates, but in many interesting situations, the density-driven error dominates. Examples include electron affinities, dissociation of molecules into charged fragments, transition state barriers, and ions and radicals in solution. In these abnormal cases, the error can be greatly reduced by using a more accurate density. A small gap between occupied and unoccupied orbitals may indicate a substantial density-driven error.

Each year, at least 10,000 calculations of the electronic structure of atoms, molecules, and solids, using Kohn-Sham (KS) density functional theory (DFT) [1], are reported[2]. In all such calculations, a small but vital part of the total energy, called the exchange-correlation (XC) energy, is approximated. In any DFT calculation, one can consider the error as arising from two distinct sources. The Euler equation minimizing the total energy gives rise to a self-consistent equation for the density involving the functional derivative of the energy[3]. In KS-DFT, these are the celebrated KS equations[1] and include the XC potential. Insertion of the solution density into the original energy functional yields the approximate energy. We write the error in an energy as the sum of two terms:

$$\Delta E = \Delta E_F + \Delta E_D. \quad (1)$$

The functional error, ΔE_F , is the contribution due to approximating the energy functional, while ΔE_D is the density-driven error due to the error in the self-consistent density. Under typical circumstances of KS calculations, self-consistent densities are extremely accurate, and the error in such *normal* calculations is dominated by ΔE_F . The functional error of well-known approximations for given properties of given systems has become known from experience[4], and can often be rationalized[5]. More sophisticated approximations are often tested using the densities (and orbitals) from less-sophisticated ones[6], a practice that assumes the calculation is normal.

But in a small fraction (but still a very large number) of calculations, ΔE_D dominates over ΔE_F . These errors can be greatly reduced by using more accurate densities. More importantly, the large energy error is typically misclassified as being due to a limitation of the functional approximation, rather than the abnormality of the calculation. The infamous self-interaction error (SIE) [7] made by standard DFT approximations for small atomic anions is so large that the ground-state is not even bound[8, 9]. In fact, these are abnormal calculations and electron affinities with standard approximations evaluated on better densities are extremely accurate[10, 11].

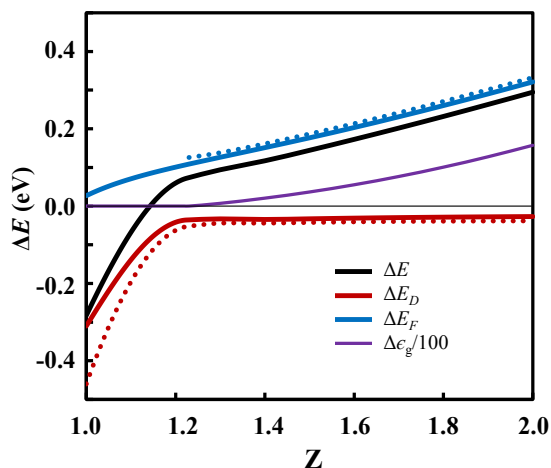


FIG. 1. Errors in ground-state energies of two-electron ions as a function of nuclear charge: PBE energies evaluated on exact[12, 13] (solid) and Hartree-Fock (HF, dotted) densities.

Fig. 1 shows the paradigm of a catastrophic density-driven error, the two-electron ion as a function of Z , the nuclear charge. As has long been known[14], as Z is reduced from 2 (He) to 1 (H^-), a fraction of an electron unbinds (about 0.3) in a standard DFT calculation[15], leading to an increasing error with decreasing Z (solid black line). But the solid colored lines show that, around $Z_c \approx 1.23$, where the orbital energy vanishes and the system begins to ionize, it is the density-driven error that is growing, and leads to the qualitative change in ΔE . The functional error is almost zero for H^- and is far less than for He. A DFT calculation with an accurate two-electron density produces a smaller error for the electron affinity of H than for the ionization energy of He[10].

In this letter, we show that (i) abnormality is a general phenomenon that can affect broad classes of DFT calculations, from two-electron ions to radicals in solution, (ii) more accurate densities qualitatively improve such calculations, (iii) a small (or zero) HOMO-LUMO gap in the approximate DFT calculation is an indicator of a density-driven error, and (iv) HF densities are sufficient to cure many density-driven errors.

We begin with a more detailed definition of Eq. (1). Let E be the exact energy of a system and $n(\mathbf{r})$ its electronic density. Let \tilde{E} and $\tilde{n}(\mathbf{r})$ be their analogs in the approximate calculation. Then

$$\Delta E_F = \tilde{E}[n] - E[n], \quad \Delta E_D = \tilde{E}[\tilde{n}] - \tilde{E}[n]. \quad (2)$$

Since only the XC contribution is approximated in KS-DFT, $\Delta E_F = \tilde{E}_{\text{xc}}[n] - E_{\text{xc}}[n]$. We apply our definition to both total energies and energy differences.

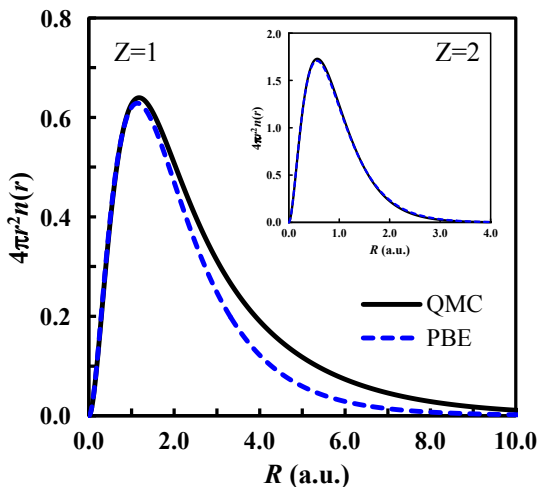


FIG. 2. Exact and PBE radial densities for H^- and He.

Most DFT calculations use either a generalized gradient approximation (GGA) [15] or a hybrid functional [16, 17]. The functional error is transmitted to the density via the XC potential, $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}} / \delta n(\mathbf{r})$. For these standard approximations, which contain SIE, a well-known failing is that $v_{\text{xc}}(\mathbf{r})$ decays too rapidly with r , so that the overall KS potential is too shallow [18]. For normal calculations, the KS eigenvalues are insufficiently deep, by several eV. However, a constant shift in the potential has no effect on $\tilde{n}(\mathbf{r})$, which is very accurate, as seen in the inset of Fig. 2. This is quantified by the magnitude of ΔE_D in Fig. 1 for $Z = 2$. Thus, normally, the SIE in the potential produces little error in the total energy.

In an *abnormal* calculation, the system is peculiarly sensitive to the error in $v_{\text{xc}}(\mathbf{r})$, so that the $\tilde{n}(\mathbf{r})$ differs significantly from $n(\mathbf{r})$, enhancing ΔE_D . To make Fig. 1, we carefully interpolated accurate QMC energies [12, 13] from $Z^{-1} = 1$ to 0, and repeated this procedure applying PBE to the exact densities to find $\Delta E_F(Z)$. We also used Turbomole [19] to solve for self-consistent PBE energies and the eigenvalue. For $Z \leq Z_c$, the eigenvalue is pinned to 0, and an increasing fraction of an electron escapes. To achieve self consistency, we decrease the occupation of the orbital from 2 until we find an occupation at which the total energy converges and the eigenvalue vanishes. The large error in density is very visible in Fig. 2, where the PBE density integrates to only 1.7 electrons, so that all energy components, especially the

Hartree energy, are quite inaccurate. Because of the variational principle, the total energy remains more accurate than any of the individual components. From Fig. 1, one sees that PBE is (somewhat accidentally) almost exact for H^- when evaluated on the exact density. This illustrates the basic difference between normal and abnormal calculations: Normally, improving the density has only a negligible effect on performance; in an abnormal calculation, it can qualitatively improve results.

Our method for classifying DFT errors is general. Declaring a calculation abnormal depends on both the energy being calculated (total, ionization, bond, etc.) and the approximation being used. The error in *any* approximation can be studied in this way. We focus here on the SIE of standard approximate functionals because of its ubiquity, but one can apply the same reasoning to, e.g., the correlation error in optimized effective potential (OEP) exact exchange calculations [20], or the error in the KS kinetic energy in orbital-free approximations [21]. Much recent research is focussed on localization errors of approximations [22]. The classic examples of stretched H_2 and H_2^+ are normal, because self-consistent densities (restricted in the case of H_2) are not so different from exact densities. More complex situations should be re-examined.

We do not always need an extremely accurate density to eliminate density-driven errors, merely a density that is substantially more accurate than the abnormal density of the DFT calculation. For atomic and small molecular anions, a simple HF calculation is often sufficient to largely eliminate the density-driven error of standard DFT approximations. DFT energies evaluated on HF densities, called HF-DFT [10], yield more accurate electron affinities than DFT ionization potentials [11].

An indicator of a likely density-driven error is given by the HOMO-LUMO gap in the approximate calculation. Apply linear response theory to the KS system:

$$\delta n(\mathbf{r}) = \int d^3r' \chi_s(\mathbf{r}, \mathbf{r}') \delta v_s(\mathbf{r}') \quad (3)$$

where $\delta n(\mathbf{r})$ is the change in density induced by $\delta v_s(\mathbf{r})$,

$$\chi_s(\mathbf{r}, \mathbf{r}') = \sum_{i,j} (f_i - f_j) \frac{\phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}') \phi_j(\mathbf{r}')}{\epsilon_i - \epsilon_j + i0_+} \quad (4)$$

is the static density-density KS response function, and $\phi_i(\mathbf{r})$, ϵ_i , and f_i are the KS orbitals, eigenvalues, and occupation factors, respectively [3]. Since the occupation factors determine that i only includes occupied orbitals while j sums over only unoccupied orbitals, the smallest denominator (and hence the largest contribution) is from the transition from the highest occupied KS orbital to the lowest unoccupied one, called the HOMO-LUMO transition. Normally, the difference between the exact and approximate KS potentials is small, ignoring any constant shift. If the approximate HOMO-LUMO gap

($\Delta\epsilon_g$) is not unusually small, this error leads to a small error in density. But if $\Delta\epsilon_g$ is small, even a small error in the KS potential can produce a large change in the density, and self consistency only increases this effect. Thus small $\Delta\epsilon_g$ suggest large density errors, and we include the gap in Fig. 1. For two-electron ions, the PBE LUMO is unbound, so that $\Delta\epsilon_g = |\epsilon_{HOMO}|$. At Z_c this vanishes. For atomic anions in general, the HOMO of the PBE potential on the exact density has a positive energy, i.e., a resonance[10]. Finite-basis atom-centered calculations turn this resonance into an eigenstate, making small density-driven errors, and produce accurate electron affinities[23].

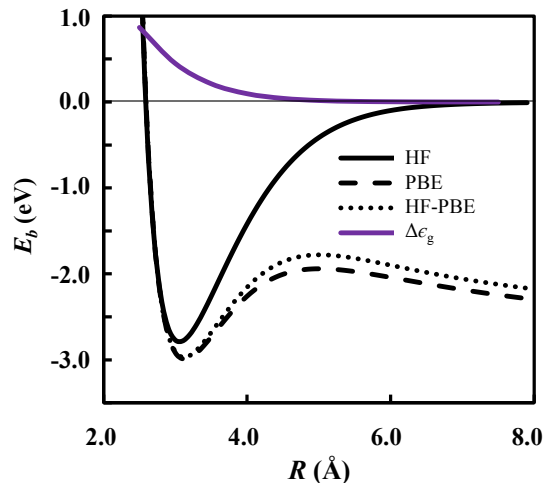


FIG. 3. Energy of H_2^+ as a function of separation in several calculations, and the PBE HOMO-LUMO gap.

However, a small gap does not always imply a density-driven error. Consider the classic example of a severe SIE, namely stretched H_2^+ with a standard functional[22], as shown in Fig. 3. The small gap suggests abnormality, but when a HF-DFT calculation is performed, the error barely changes. Thus, this is a normal calculation, these errors are functional-driven, not density-driven, and HF-DFT is not recommended.

Our next abnormality is well-known[24]. DFT calculations of molecular dissociation energies (E_b) are usefully accurate with GGA's, and more so with hybrid functionals. These errors are often about 0.1 eV/bond[25], found by subtracting the calculated molecular energy at its minimum from the sum of calculated atomic energies. This is because, if one simply increases the bond lengths to very large values, the fragments fail to dissociate into neutral atoms. The prototypical case is NaCl, which dissociates into $Na^{0.4}$ and $Cl^{-0.4}$ in a PBE calculation[24]. The large error in density for the stretched bond yields $\Delta E_b \approx 1$ eV, as shown as the difference between PBE and HF-PBE in Fig. 4. In this case, the HF density spontaneously suddenly switches to neutral atoms at about 5.6 Å, but is correct in the dissociation limit. The common practice of using isolated atomic calculations is in-

consistent, but removes the density-driven error, because isolated atoms are normal. Incorrect dissociation occurs whenever the approximate HOMO of one is below the LUMO of the other[24], which guarantees a vanishing $\Delta\epsilon_g$ when the bond is greatly stretched. The exact $v_{xc}(\mathbf{r})$ contains a step between the atoms that ensures correct dissociation, but which is missed by semilocal approximations.

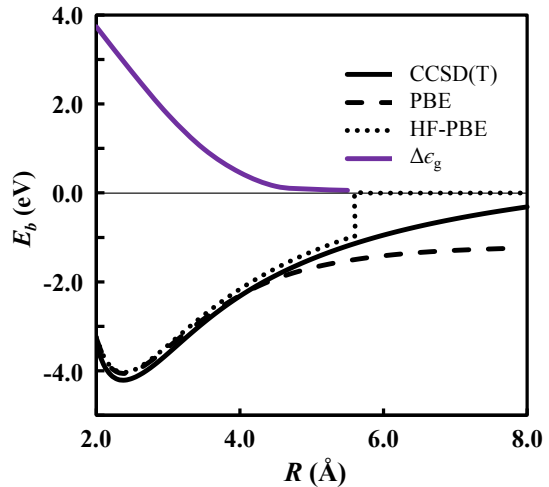


FIG. 4. Energy of NaCl as a function of Na-Cl distance in several calculations, and the PBE HOMO-LUMO gap.

When modern functionals were first being adopted for molecular calculations, they were sometimes evaluated on HF densities[26, 27], so as to compare only functional errors. More recently, Janesko and Scuseria[28] showed this led to substantial improvement in transition-state barriers. The prototype of such barriers is the symmetric H-H₂ transition state, which is improved by almost a factor of 2 by using HF-PBE instead of PBE. Here $\Delta\epsilon_g^{PBE}$ is not quite as small (2.5 eV) as in other cases, but the improvement upon using the HF densities is still substantial. High-level *ab initio* calculations yield an energy barrier of 0.43 eV[28], where PBE gives value of 0.16 eV and HF-PBE gives 0.25 eV. Analysis of a collection of barriers in Table 1 of Ref. 29 shows that, in cases where the HF-DFT barrier differs from the self-consistent barrier by more than, for instance 25%, the mean absolute error is more than three times smaller than DFT, with the sole exception of t-N₂H₂ hydrogen transfer forward reaction barrier, where HF density is spin-contaminated (just as in the molecule CN[11]).

Finally we report new applications where we drive out the density-driven error. We investigate potential energy surfaces (PES) of odd-electron radical complexes like OH·Cl⁻ and OH·H₂O. These are important in radiation, atmospheric, and environmental chemistry, as well as in cell biology[30-33]. For example, the behavior of anions in droplets is critical to our understanding aerosols in atmospheric chemistry[34]. Accepted wisdom claims that anions near an air-water interface, being less

screened, have lower concentrations[35]. But recent classical molecular dynamics (MD) simulations have shown the opposite[35, 36]. This controversy invites an *ab initio* MD approach, to either reinforce or debunk the classical simulations.

However, DFT approximations have problems with these systems[37–40]. Several such PES studies show two minima in the ground-state PES. One is a hydrogen-bonding structure while the other is a 2-center, 3-electron interacting hemi-bonding structure[41]. High-level quantum chemical calculations[41] and self-interaction corrected DFT results[40, 42] reveal that the true PES has only one minimum, the hydrogen-bonding structure. The hemibonding structure is relatively overstabilized in approximate DFT because three electrons are incorrectly delocalized over two atoms.

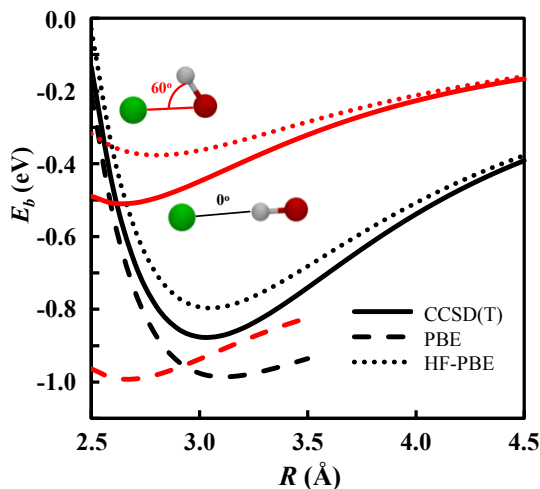


FIG. 5. Potential energy surface scans for the $\text{HO}\cdot\text{Cl}^-$ complex along $\text{Cl}-\text{O}-\text{H}$ angle of 0° (hydrogen-bonding structure, black lines) and 60° (hemi-bonding structure, red lines) using various methods; R is the $\text{Cl}-\text{O}$ separation.

In Fig. 5, we show plots of the PES of $\text{HO}\cdot\text{Cl}^-$ complex using different methods. The $\text{O}-\text{H}$ bond length was fixed at 1 Å. The binding energy is

$$\Delta E_b = E_{\text{HO}\cdot\text{Cl}^-}(R, \theta) - (E_{\text{HO}} + E_{\text{Cl}^-}), \quad (5)$$

where $E_{\text{HO}\cdot\text{Cl}^-}(R, \theta)$ is the energy on a given geometry with $\text{Cl}-\text{O}$ distance R , and $\text{Cl}-\text{O}-\text{H}$ angle θ , E_{HO} is the energy of the OH radical, and E_{Cl^-} is the energy of Cl^- anion. The difference between the energy minima of hydrogen- and hemi-bonding structures in PBE is less than 0.01 eV. A small $\Delta\epsilon_g$ of PBE in the hydrogen bonding structure (~ 0.32 eV) suggests a large density-driven error. We find HF-PBE follows the same trends and produces the same minima as CCSD(T), although the binding energies themselves have errors of up to 0.09 eV. We also scanned the PES of the $\text{HO}\cdot\text{H}_2\text{O}$ complex. The minimum geometry of hydrogen- and hemi-bonding structures is shown in Fig. 6. Self-consistent

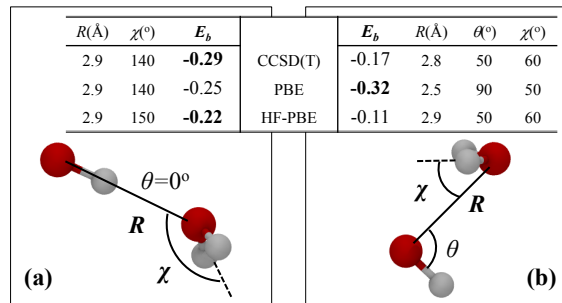


FIG. 6. Binding energies in eV of $\text{HO}\cdot\text{H}_2\text{O}$ calculated with various methods for (a) hydrogen-bonding structure and (b) hemi-bonding structure.

PBE greatly overstabilizes the hemi-bonding region, resulting in a strong, unphysical hemi-bonding minimum. CCSD(T) and HF-PBE, on the other hand, give an intuitively appealing hydrogen-bonding geometry as the global minimum. But $\Delta\epsilon_g$ of PBE is less than 1 eV, and HF-PBE fixes the problem.

To summarize, we have shown how all approximate DFT calculations can be analyzed, to check for density-driven errors. In the case of SIEs of commonly-used functionals, use of HF (or better) densities can often greatly reduce such errors. This would allow distinctions between true SIE (i.e., large energy errors even on exact densities) versus density-driven errors, which are system- and property-dependent.

Calculation details – For evaluation of DFT and HF self-consistent densities in Fig 1 and 2, aug-cc-pV6Z basis set[43] was used. From Fig 3 - 6, all calculations were performed with aug-cc-pVTZ[44–46] basis with Turbomole.

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